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published in

NIC Symposium 2004, Proceedings,
Dietrich Wolf, Gernot Münster, Manfred Kremer (Editors),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. **20**, ISBN 3-00-012372-5, pp. 91-99, 2003.

http://www.fz-juelich.de/nic-series/volume20

Magnetic Interactions in Metal Clusters: Magneto-Structural Correlations Based on Simple Model Systems

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The synthesis of molecular magnetic clusters is highly desirable, since they are the key to single molecular magnets. In order to design such molecules one needs to know suitable synthetic routes and the influence of the building units on the structural and electronic properties of the resulting molecular cluster. Of particular interest in this respect are relevant quantitative correlations between the parameters of the constituting building blocks and the magnetic properties of the molecular cluster. In this context quantum chemical calculations based on density functional theory are performed on relevant model systems. We are particularly interested in three basic bonding situations found for the aggregation of molecular magnetic units: (1) Single atom bridges like in metal oxides or polyoxometalates. (2) Hydrogen bonding which can be found in the aggregation of molecular and polymeric coordination compounds. (3) Molecules as bridging ligands between metal centers as they are found in metalloproteins.

1 Introduction

Molecular compounds with high-spin ground states represent a major goal of current research in the field of molecular magnetism. This is mainly driven by the potential applications of single-molecular magnets (SMMs) which are part of this family of compounds[1]. Examples known today are solely based on high-nuclearity transition metal compounds. Unfortunately, large molecular clusters are almost invariably obtained in a serendipitious manner from self-assembly reactions and general strategies for the synthesis of large clusters with predetermined structures and properties have not yet been developed. There are two ingredients necessary for the desired superparamagnetic behavior of such high-nuclearity compounds: the strong exchange interaction between individual spins yielding a high-spin ground state and the magnetic anisotropy of the system.

A key feature in this respect is the knowledge of magneto-structural correlations which would allow the deliberate design of magnetic systems with desired properties. The basic importance of such magneto-structural correlations is related to the concept of magnetic building blocks in the construction of molecular based magnetic systems[2,3]. In the last decades magneto-structural correlations both qualitative and quantitative have been established for several systems[4–10]. The common ground for all these correlations is given by the well-known Goodenough-Kanamori rules which are based on the interaction between pairs of natural magnetic orbitals[11]. The general problem to establish such correlations is twofold: the number of samples accessible is limited and one needs to have some inspira-

tion to find the right structural parameters for the correlation. In addition to the magneto-structural correlations also the knowledge of the underlying mechanisms of the exchange coupling interactions is important for both the interpretation and the future design of magnetic interactions. To this end theoretical methods based on the density functional theory (DFT) are most suited and well established[12]. Of particular importance is the so-called broken symmetry formalism, that allows the calculation of the energies of singlet states, which is in contrast to the calculation of the high spin state a tricky task[13–16].

We are especially interested in magneto-structural correlations due to their relevance for two important research fields, i.e. the understanding of magnetic interactions within active sites of enzymatic systems and the concepts needed to generate molecular magnetic materials. In both cases the interactions of neighboring magnetic units is decisive, since in such systems no long range interactions are observed[17,18]. Consequently the magnetic properties of pairs of magnetic building blocks are important to understand for the deliberate buildup of larger aggregates. Along this line we investigate magneto-structural correlations for representative simplified general model systems. This investigations are intended for three basic types of interactions found in aggregation of molecular magnetic units related to the following examples: (1) Single atom bridges like in metal oxides or polyoxometalates – binuclear oxovanadium(IV) compounds. (2) Hydrogen bonding which can be found in the aggregation of molecular and polymeric coordination compounds – hydrogen bonded binuclear copper(II) compounds. (3) Molecules as bridging ligands between metal centers as they are found in metalloproteins – imidazolate bridged binuclear copper(II) compounds which can model the active site of superoxide dismutase (SOD).

2 Computational Methods

DFT calculations are particularly suited, since they can not only provide detailed information on the electronic structure, but also allow easy access to energetic parameters like the magnetic exchange coupling constant J. Here the *broken symmetry formalism* is a useful tool accessible through the DFT framework. This method is well-established and has been applied to several transition metal systems[5,15,16,19]. If the broken-symmetry formalism is utilized, it is possible to express the singlet-triplet gap of exchange coupled systems with one unpaired electron per center as $J = E_{\mathrm{B}} - E(S = 1)$[14] where E_{B} is the energy of the broken-symmetry state. This procedure is in keeping with the proposal of Perdew, Savin and co-workers[20], who suggested that the broken-symmetry single determinant is the correct solution of the Kohn-Sham equations for the singlet state. Moreover, this not only holds for systems with two coupled electrons. The singlet sate can be approximated as outlined by the broken-symmetry state and the high spin state can be easily calculated by DFT methods, since this is a electronically pure state.

An important question is the choice of a proper density functional, since this determines the accuracy of the results. For this purpose the so-called hybrid methods, which combine Hartree-Fock(HF)-type and DFT-type contributions, are particularly suited[5,15,16,19]. So far the method of choice is the b3lyp hybrid method developed by Becke[21]. The good performance of these methods is consistent with the generally observed overestimation of the stabilization of the singlet state relative to the triplet state by DFT methods, because this effect is compensated by the inclusion of Hartree-Fock(HF)-type contributions, which are known to usually overestimate the relative stability of the triplet state[14]. In addition not

only energetic accuracy is important, but also the option of having a theoretical framework that allows for an easy and particularly straight forward analysis and interpretation of the results. This can be achieved by non-hybrid DFT calculations with the appropriate analytical tools as they are implemented in the ADF program package[22,23].

All calculations have been performed at the computer center (ZAM) of the Forschungszentrum Jülich utilizing two massively-parallel computers (CRAY T3E-600 and CRAY T3E-1200) and a vector-parallel computer (CRAY SV1ex). The computer system used for a particular application depends on the efficiency of the implemented software and the size of the molecular assembly to be calculated. For calculations based on the ADF program package the newly established massively-parallel IBM supercomputer JUMP is utilized.

3 Magnetic Interactions in Oxovanadium(IV) Clusters

Polynuclear transition-metal systems and especially their magnetic properties have become a subject of considerable interest in the last few years[25]. Although interesting magnetic properties have been discovered for several systems, the detailed analysis of the magnetochemistry of such polynuclear transition-metal systems continuous to be a field of growing interest[26]. In particular well-characterized oxovanadium(IV) clusters for which the magnetic properties have been analyzed are still rather rare[27,28]. Here, the recently given classification for binuclear systems with $\{\mathrm{VO}(\mu_2\text{-OR})_2\mathrm{VO}\}^{2+}$ core provides a valuable tool,

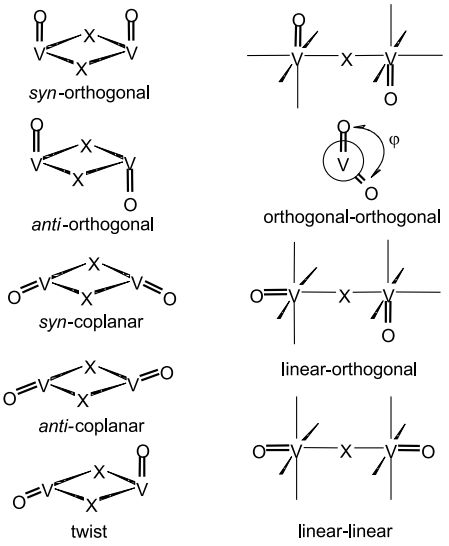

Figure 1. Possible configurations of the two terminal oxo-groups for binuclear vanadium(IV) units with single atom bridges which establish edge- (left) and vertex-shared bridging modes (right). The arrangements are classified according the orientation of the oxo-groups with respect to the bridging plane in the case of edge-sharing units (orthogonal, coplanar, twist) or the connecting single atom bridge for vertex-sharing units (linear, orthogonal) and the orientation of the two terminal oxo-groups (*syn*, *anti*) (see ref. 24).

as it shows a correlation with the observed magnetic properties[5]. This magneto-structural relationship is particularly appealing since edge-shared binuclear units are one of the basic structural motifs found in polynuclear oxovanadium(IV) clusters.

Given the clear coordination requirements set up by the vanadyl group the reported magneto-structural relationship[5] can be generally applied to edge-shared binuclear units independent of the actual coordination mode at the individual oxovanadium(IV) centers, i.e. octahedral or square pyramidal. Therefore, only the relative orientation of the vanadyl groups within a binuclear unit is necessary to qualitatively predict its magnetic behavior in terms of antiferro- (*syn*- and *anti*-orthogonal and *syn*-coplanar) or ferromagnetic interactions (*anti*-coplanar and twist) between the metal centers. Although a different notation is necessary, this concept can basically be extended to oxovanadium(IV) centers in a vertex-shared bridging mode, which is yet another fundamental structural motif in the construction of polynuclear oxovanadium(IV) clusters[29]. The resulting generalized classification schemes for both edge- and vertex-sharing binuclear units with single atom bridges are depicted in figure 1. Similar considerations as those used to account for the magnetic behavior of edge-sharing binuclear oxovanadium(IV) complexes[5] can be applied to predict the magnetic interactions operative in the case of vertex-sharing binuclear units. Consequently, two of the possible configurations should lead to ferromagnetic interactions, namely the linear-linear and linear-orthogonal ones, whereas the orthogonal-orthogonal configuration depending on the dihedral angle φ can either yield antiferro- or ferromagnetic interactions, with the latter expected for φ near 90°. Within the scheme for vertex-shared binuclear units the configurations also include the situations where one of the oxo-groups is at the bridging position X yielding either oxo bridged units[30] or extended chains[31]. Consistent with the classification schemes given in figure 1 the predominant magnetic exchange interactions observed for polynuclear oxovanadium(IV) clusters are of antiferromagnetic nature[27,28].

The calculations performed confirm that the computational strategy employed, which is based on the DFT approach, provide good estimates for the experimental coupling constants of the investigated binuclear oxovanadium(IV) complexes[5,24,32]. Therefore, this methodology permits the investigation of several structural effects based on variations of simple binuclear model systems containing the common $\{\mathrm{VO}(\mu_2\text{-}\mathrm{OH})_2\mathrm{VO}\}^{2+}$ core. The results confirm that different exchange mechanisms are operative within this core framework. Two basic types can be identified, a through-space mechanism with direct orbital interaction of the metal centers in the orthogonal configurations and a superexchange mechanism in the case of the coplanar configurations. This immediately directs the possible ferro- or antiferromagnetic interaction between the metal centers. An interesting finding is the influence of the geometry around the bridging oxygen atom on the coupling constant, that can induce an alternation of the nature of coupling. Similar effects have been found for binuclear copper(II) compounds, but with a much larger dependence on the variation of the structural parameters.

4 Magnetic Interactions in Supramolecular Aggregates

Hydrogen bonds are the master key interaction in biological structures, supramolecular chemistry, and crystal engineering[33]. As such they are also important in order to understand the properties of relevant magnetic materials[18]. In particular for some copper(II) containing coordination compounds it has been shown that the variation of possible supramolecu-

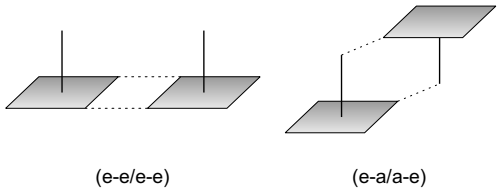

Figure 2. Schematic representation of possible bridging patterns observed for binuclear copper(II) complexes with two hydrogen bonds between the metal fragments.

lar interactions can substantially influence the magnetic properties of related coordination polymers[34].

Although copper(II) complexes have been widely studied, for binuclear units only two basic patterns of hydrogen bonding have been observed (see fig. 2). According the preferred square planar coordination environment for copper(II) ions with the option of one or two additional apical ligands, these hydrogen bridges can be denoted as either equatorial-equatorial (e-e) or equatorial-apical (e-a) corresponding to the position of the involved donor and acceptor atoms. Given the magnetic orbital at each copper(II) center as defined by the short equatorial bonds, i.e. basically an orbital of $d_{x^2-y^2}$ type with some possible admixture of d_{z^2} character, a qualitative magneto-structural correlation would predict antiferromagnetic coupling for (e-e/e-e) bridging patterns and weak interaction with possibly ferromagnetic nature for (e-a/a-e) bridging patterns. In addition, the magnitude of the magnetic coupling should also be related to the strength of the involved hydrogen bridges. This basic concept is in agreement with the observed structural and magnetic data of the relevant systems known[35].

An extension to this qualitative magneto-structural relationship is given by the copper(II) complexes with the trivalent, pentadentate Schiff base ligand N-salicylidene-2-(bis(2-hydroxyethyl)amino)ethylamine (H_3sabhea). The resulting self-complementary

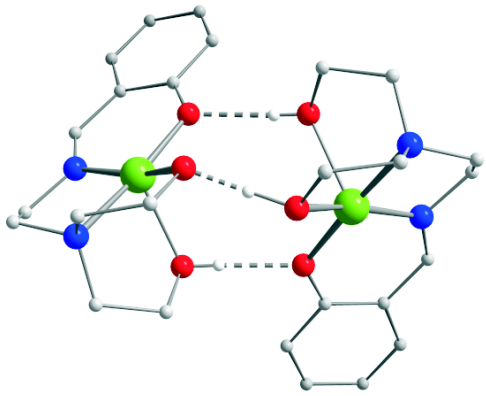

Figure 3. Structure of the first threefold hydrogen bridged binuclear copper(II) complex **2**; color code: copper (green), oxygen (red), nitrogen (blue), carbon (gray).

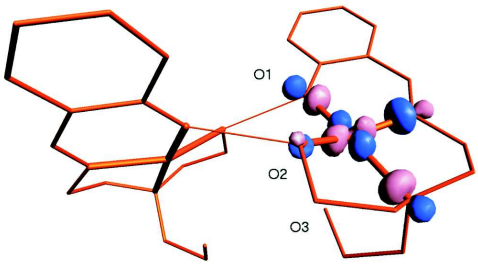

Figure 4. Representation of the magnetic orbital of the cationic binuclear copper(II) complex **1**; the two hydrogen bonds are represented by the small lines.

complex cation $[Cu(H_2sabhea)]^+$ can be isolated as hydrogen bridged binuclear complex **1**, which can be reversibly deprotonated in aqueous solution yielding **2** (see fig. 3)[19].

$[\{Cu(H_2sabhea)\}_2](BF_4)_2$ (**1**)

$[\{Cu(H_2sabhea)\}\{Cu(Hsabhea)\}]BF_4$ (**2**)

With DFT calculations utilizing the broken-symmetry formalism, it is possible to reproduce the experimental exchange coupling constants in excellent agreement[19]. Therefore, this methodology permits the investigation of geometrical effects of relevant model systems on their exchange coupling interaction. The magnetic orbitals as derived from the broken-symmetry calculations have basically $d_{x^2-y^2}$ character with contributions from the equatorial oxygen and nitrogen atoms (see fig. 4 and 5). This is consistent with the observed distorted square pyramidal coordination geometry at the copper(II) centers. The reduced exchange coupling constant for **2** as compared to **1** indicates that only hydrogen bridges of the (e-e) type are effectively transmitting exchange interactions be-

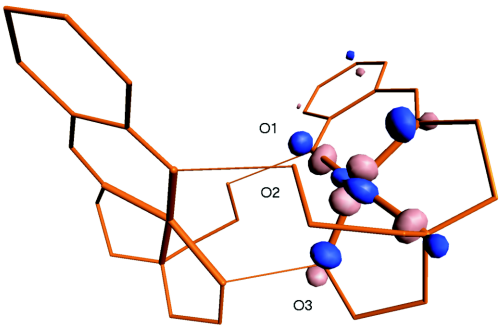

Figure 5. Representation of the magnetic orbital of the cationic binuclear copper(II) complex **2**; the three hydrogen bonds are represented by the small lines.

tween the copper(II) centers, i.e. both the hydrogen donor and the hydrogen acceptor must have contributions to the respective magnetic orbital (see fig. 4 and 5). Moreover, according to a magneto-structural correlation based on the O$\cdots$O distance of hydrogen bridged copper(II) complexes that was derived from a theoretical study on the model system [{Cu(OH)$(NH_3)_2(H_2O)\}_2$][36], both complexes **1** and **2** should exhibit much larger exchange coupling constants in the range of -80 to -100 cm^{-1}. This is indicative for the importance of the relative orientation of the magnetic orbitals with respect to each other, which for **1** and **2** is unfavorable as compared to the coplanar orientation of the model system used for the theoretical study[36].

An interesting difference as the magnetic orbitals are concerned is found in the contribution of the coordinated ligand. In the case of the threefold bridged complex **2** the aromatic ligand system has a larger contribution. Consequently, the variation of the substitution pattern at the aromatic ring system is found to influence the magnetic coupling between the copper(II) centers in a different manner for both complexes. Nevertheless, the corresponding oxygen atom O1 only permits effective magnetic interactions in the case of complex **1** (see fig. 4 and 5).

An interesting finding is the fact, that the generally observed superexchange interaction found for the hydrogen bonded copper(II) complexes is due to a direct through-space interaction between the oxygen atoms involved. Therefore, a simple magneto-structural correlation based on a hydrogen bond length criterion is not sufficient. On the contrary the key factor is given by the hydrogen bonding pattern. Whereas the fine tuning of the magnetic properties is related to the hydrogen bonding distances and the relative orientation of the magnetic orbitals of both copper units with respect to the hydrogen bonding pattern.

5 Magnetic Interactions through Bridging Ligands in Metalloproteins

Imidazole is an important ligand in biological systems, since the imidazole moiety of the histidyl residues in a large number of metalloproteins constitutes all or part of the binding site of various transition metal ions[37]. For instance, its conjugate base, the imidazolate anion, is known to act as a bridging ligand between copper(II) and zinc(II) ions in bovine erythrocyte superoxide dismutase (BESOD)[38,39]. In addition, imidazolate as a bridging

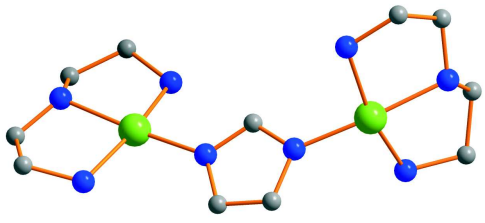

Figure 6. Structures of a binuclear copper(II)complex with an imidazole as bridging ligand; color code: copper (green), nitrogen (blue), carbon (gray).

ligand has also been employed in the synthesis of magnetic coordination polymers of various dimensionality[40]. In this context the investigation of magnetic exchange interactions through imidazolate bridges brings up the question of possible correlations between structure and magnetic properties.

Although a series of relevant homo binuclear copper(II) complexes has been reported in the literature, so far no magneto-structural correlation could be established[41]. Moreover, even the differentiation between possible magnetic exchange pathways through the imidazolate ligand is still an unsolved question. In order to probe the factors influencing structure and magnetism of such complexes we study substituted μ-imidazolato bridged binuclear complexes (see Figure 6).

DFT calculations on the relevant model systems are performed, that allow for a deliberate variation of structural parameters in order to trace their influence on the magnetic interaction between the two copper(II) centers. An important question at this point is whether and how far the large systems can be simplified so that they can still represent the individual molecular system under investigation. This is related to the question of how particular bridging ligands can propagate magnetic exchange and how important the electronic influence of more distant substituents can be. This knowledge may enable to set up new rules for a more deliberate design of new magnetic molecular clusters. Based on the results obtained thus far, it can be concluded that the magnetic interactions between the copper(II) centers is dominated by the σ exchange pathway through the bridging imidazolate ligand.

Acknowledgments

This project is supported by a grant of computer time of the John von Neumann Institute for Computing (NIC) and a research grant of the Deutsche Forschungsgemeinschaft.

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